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54 **Phosphated, oxidized starch and use of same as dispersant in aqueous solutions and coating for lithography.**

57 A novel phosphated, oxidized starch having a molecular weight of about 1,500 to about 40,000 Daltons, a carboxyl degree of substitution of 0.30 to 0.96, and a phosphate degree of substitution of from about 0.0002 to about 0.0005, which is useful as a dispersant for aqueous, high-solid slurries of minerals and inorganic pigments, as a replacement for gum arabic in gumming and fountain solutions for lithography, and as a drilling fluid additive.

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PHOSPHATED, OXIDIZED STARCH AND USE OF SAME AS DISPERSANT IN AQUEOUS SOLUTIONS AND COATING FOR LITHOGRAPHY

This invention relates to a phosphated, oxidized starch that is useful, for instance, as a dispersant in aqueous, high-solid slurries of minerals and inorganic pigments, as a substitute for gum arabic in gumming and fountain solutions for lithography, and as an additive to drilling fluids.

Dispersants are conventionally used to control the rheology of high-solid systems containing pigments and filler such as latex paints, joint cements, drilling muds, paper coating colors and paper coatings. The dispersants most widely used for this purpose are low molecular weight anionic polymers containing a multiplicity of carboxylate, sulfonate, phosphonate or phosphate groups. High-solid cakes or pastes of fillers and pigments are commonly dispersed or thinned with various polyphosphates, lignosulfonates or carboxylated polymers. The latter are often polymers of salts of acrylic or maleic acids or their various copolymers, or carboxylated polysaccharides such as low molecular weight sodium carboxymethyl cellulose (CMC).

Such anionic dispersants are believed to adsorb on the surface of fillers such as clays and pigments to provide a negative charge to the filler surface or enhance it. Mutual repulsion between like charged particles then serves to separate filler particles and keep them from reagglomerating.

In paper manufacture, clays and pigments are supplied to paper mills in predispersed form, using anionic dispersants in high-solid slurries. The repulsive forces that separate the particles can then be counteracted using cationic retention aids to precipitate the clays and pigments onto the paper stock.

While polymeric orthophosphates are effective dispersants for many particulates, and have application where dispersed particulates need to be reflocculated or reagglomerated as in paper manufacture, their hydrolytic instability, causing loss in dispersancy, and tendency to bloom to the surfaces of coatings are disadvantages. Monomeric orthophosphates, the end hydrolysis product of polyphosphates, are not very efficient dispersants compared to polyphosphates.

Synthetic polyanionics, such as the polyacrylates, are not as susceptible to hydrolysis, but their high charge density and persistence can be a disadvantage in applications where dispersed particulates need to be reflocculated or reagglomerated, as is necessary in paper manufacture, and they require excessive amounts of cationic retention aids.

Lignosulfonates are used principally as thinning dispersants in clay-based drilling muds, but their dark color inhibits use in applications where color and brightness are important, such as in paper manufacture.

Dispersants containing oxidized and depolymerized starch having molecular weights of 200,000 and about 100,000 Daltons, with and without the addition of phosphate esters of depolymerized starch, are known and have been used in combination with low molecular weight CMC to disperse gypsum or phosphogypsum suspensions, as disclosed in German Patent Application No. 32030 67. The lower molecular weight composition, which is hot-water soluble but insufficiently oxidized to be soluble in cold water, is the more effective gypsum dispersant. However, according to the Application, when used alone, the starch phosphate tends to flocculate the suspension.

Oxidized starch compositions have been used to improve detergency in soaps and detergents by sequestering calcium cations, for instance as disclosed in U.S. Patent 3,629,121.

There is a need for improved oxidized starch compositions, which may be used as dispersants for clay, titanium dioxide, calcium carbonate, minerals, inorganic pigments, and other particulates in high-solids aqueous systems, and also as detergent builders and to replace for gum arabic in lithography. There is no disclosure in the above publications of oxidized starch compositions that could respond to that need.

According to the invention, an oxidized and depolymerized starch is characterized in that it is phosphated to a phosphate degree of substitution of about 0.002 to about 0.005, has a molecular weight of about 1,500 to about 40,000 Daltons, and is soluble in cold water by virtue of a carboxyl degree of substitution of 0.30 to 0.96.

Normally, the novel phosphated, oxidized starch of this invention has about 15% to about 48% of its repeating anhydroglucose ring units cleaved between carbon atoms 2 and 3 and oxidized to carboxyl groups (i.e.) a carboxyl degree of substitution of from about 0.30 to about 0.96).

Preferably, the phosphated, oxidized starch according to the invention, has a carboxyl degree of substitution of 0.44 to 0.50.

Also preferably, the phosphated, oxidized starch has a phosphate degree of substitution of about 0.003 to about 0.005, more preferably, a phosphate degree of substitution of about 0.004 to about 0.005.

Also preferably, the phosphated, oxidized starch has a molecular weight of about 5,000 to about 30,000,

most preferably 15,000 to 20,000 Daltons.

Phosphate is naturally present in all biological systems (as an energy exchange medium). For instance, corn starch can contain up to 0.015%, by weight, of unextractable phosphorus (a phosphate degree of substitution of about 0.00078). This invention is directed to use of phosphate in an amount substantially greater than that naturally present in such biological systems. The phosphate degree of substitution is calculated as if only monomeric phosphate moieties are present, but there may be minor amounts of polymeric species (comprising, for instance, 2 or 3 phosphate moieties).

The phosphate ester group can be introduced either before the bleach oxidation of starch or afterwards. Phosphating agents for starch are well known. Phosphoric acid, phosphorous pentachloride, phosphoryl chloride as well as a number of polymeric sodium orthophosphates are among the more useful ones. An especially convenient phosphating agent for purposes of this invention is sodium trimetaphosphate, which reacts either homogeneously with concentrated solutions (15-25%) of oxidized starch or heterogeneously with unmodified starch granules in aqueous 40% slurry.

Generally, aqueous solutions prepared by bleach addition contain the phosphated, oxidized starch in an amount of about 0.01 to about 16 wt. % by weight of the total aqueous solution. The phosphated, oxidized starch can be precipitated from such aqueous solutions using methanol or acetone. The isolated product is a white granular composition (greater than 90% purity; impurities include NaCl). By precipitating and redissolving the phosphated, oxidized starch, aqueous solution containing up to about 50 wt. % by weight of the total aqueous solution, can be prepared.

The phosphated, oxidized starch of this invention can be produced by the oxidation and depolymerization of starch by reaction with sodium hypochlorite in an alkaline medium whereby the bond between carbon atoms 2 and 3 of the repeating anhydroglucose residue is cleaved and the carbon atoms are oxidized to carboxylate groups, in a conventional manner as taught for instance by Whistler and Schweiger, 79 J. Am. Chem. Soc. 6460 (1957).

The pH of the reaction medium is maintained between 7.5 and 10.0 and preferably between 8.5 and 9.0. At higher pH the reaction rate becomes sluggish, while inefficient oxidation occurs below pH 7.0. Temperatures are maintained between about 25 and 65°C and preferably between 45 and 50°C. Reaction rates below 35°C are slow. Higher temperatures occasion increasing conversion of hypochlorite into chlorate that is not an oxidant for starch.

All starches, such as corn, tapioca, sago, wheat, rice and potato starch, are suitable substrates for reaction and, depending on the extent of oxidation, gradually dissolve as oxidation proceeds in the alkaline reaction medium. In this respect, waxy maize and potato starch are especially preferred because complete granule dissolution is achieved at low conversion earlier in the reaction. High amylose containing starches, e.g., those containing 50 wt. % or more amylose, are difficult to use as they are not readily oxidized due to their inability to readily go into solution when treated with sodium hypochlorite and sodium hydroxide. Higher levels of sodium hypochlorite will eventually bring high amylose containing starches into solution.

The starch can be slurried directly in sodium hypochlorite solutions (ca. 5% as chlorine). The rate of oxidation can be controlled by temperature and correct pH can be maintained through addition of sodium hydroxide or other alkali as sodium hypochlorite is consumed in the oxidation reaction. Alternatively, sodium hypochlorite and sodium hydroxide solution can be added to concentrated (40%) slurries of starch in water. This latter method is especially preferred because the rate of this highly exothermic reaction (ca. 665 calories per gram of starch) can thus be controlled by the rate of sodium hypochlorite addition. The added degree of control attained by this technique permits the safe use of more concentrated starch slurries and stronger sodium hypochlorite solutions (approximately 12% as chlorine), both of that result in higher product concentrations in final reaction solutions.

The phosphated or unphosphated oxidized starch is recovered in the form of the alkali metal salt of the carboxylic acids formed during the oxidation procedure. The sodium or other alkali metal salts are insoluble in aqueous organic solvents such as acetone, and the corresponding free acid is soluble in water, but is also insoluble in organic solvents such as acetone. The free acid is formed from the alkali metal salts of the carboxylic acids by reaction with any strong acid such as a mineral acid, for example, hydrochloric acid.

To measure the degree to which oxidation has occurred, the amount of carboxylic acid groups on the starch molecule are measured by conventional titration techniques. In this procedure, a measured amount of phosphated or unphosphated starch that has been oxidized and exists as the sodium salt is slurried in acetone and is neutralized with an excess of a strong acid such as hydrochloric acid. This converts the sodium salt of the acid groups on the oxidized starch to the free acid form. This form of the starch is insoluble in the acetone and remains dispersed and settles to the bottom of the vessel containing the dispersion. An aliquot of the supernatant solution is then titrated with a strong base, such as sodium hydroxide (0.1 N solution) to the phenolphthalein end point. This back titration gives the amount of

rise from about 6.5 to 11.0. Thereafter, the remaining sodium hypochlorite (620 g, 1.13 mole total as Cl_2) was added from a dropping funnel at a continuous rate of 6.9 g (or 0.86 g Cl_2) per minute. A sodium hydroxide solution (13 g/100 ml water) was added from a dropping funnel at a rate sufficient to maintain the medium pH of the medium between 8.5 and 9.0 (sodium hydroxide was consumed throughout the reaction).

5 The reaction temperature was maintained at 50° C by intermittent passage of cooling water through the heating/cooling coils. As the reaction proceeded, the oxidized starch solids dissolve in the reaction medium and formed a clear to hazy, water-thin solution. After the sodium hypochlorite addition was completed, the pH was maintained at about 8.5 to 9.0 by incremental sodium hydroxide (above solution) addition and agitation was continued at 50° C until all the bleach was consumed.

10 The latter condition was indicated by constant pH over a 15 minute interval after a caustic adjustment, and by the absence of oxidizing in a negative starch-iodide test for residual bleach.

The resulting solution was an intermediate composition that could have been used to prepare a phosphated, oxidized starch per this invention. The solution was neutralized and worked-up as described below, then used as a control dispersant in example 5 below.

15 The resulting solution was neutralized with concentrated hydrochloric acid to pH 7.0 as solutions left alkaline gradually darken on standing.

Work-up consisted of precipitating the cooled (25° C) solution into 8 liters of methanol filtering out the oxidized starch, washing the filter cake solids twice with 500 ml of methanol, and then drying them at 50° C. The product had a carboxyl D.S. of 0.43.

PREPARATION EXAMPLE 2

25 This example demonstrates preparation of an oxidized starch, which can be phosphated to produce a phosphated, oxidized starch per this invention.

In a five gallon plastic bucket, equipped with air-driven Teflon paddle stirrer, a thermometer and combination pH electrode, corn starch (96 g, 0.59 anhydroglucose equivalents) was slurried in pre-chilled (20° C) sodium hypochlorite (2400 ml, 130 g Cl_2 by iodometric titration, 1.83 mole) stabilized with sodium bicarbonate (2.52 g, 0.03 mole). The reaction was initiated by adjusting the pH to 8.5 with concentrated HCl (12 N solution). As the reaction proceeded, sodium hydroxide solution (13 g Na/100 ml water) was added via a dropping funnel to maintain the pH at 8.0-8.5. The extent of reaction was monitored by measuring the temperature and quantities of base and oxidant consumed. The maximum temperature (approximately 35° C) was reached after 15 minutes. After one hour, about 90% of the base and oxidant were consumed.

35 The reaction was allowed to proceed until starch-iodide testing of solution aliquots indicated the absence of bleach oxidant (Alternatively, the reaction could have been terminated by addition of sodium metabisulfate). The product could have been used as a dispersant or as an intermediate to prepare a phosphated, oxidized starch per this invention. However, it was neutralized and worked-up as in the same manner as in Example 1. A white product (108 g, 12% moisture, 33 3% ash as Na_2SO_4 and carboxyl D.S. of 0.72) resulted.

PREPARATION EXAMPLE 3

45 This example demonstrates preparation of a phosphated, oxidized starch per this invention.

The 2 liter kettle of Example 1 was charged with a slurry of 180 parts by weight corn starch (dry basis, 1.11 anhydroglucose equivalents) containing 36 parts by weight sodium trimetaphosphate (STMP), and 450 parts by weight water. The mixture was heated to 50° C after which sodium hydroxide (13% solution) was added to adjust the pH to 11.0. Temperature and pH were maintained for one hour after which sodium hypochlorite (652 g at 12.1% Cl_2 , 1.11 mole Cl_2) and sodium hydroxide addition was carried out as described in Example 1. Neutralization and work-up by precipitating the cooled reaction solution into methanol (8 liters plus two 500 ml washes) yielded a white solid having a carboxyl D.S. of 0.42 and containing 3.6% phosphorous of which 0.06% was bound to the product in ester linkage.

PREPARATION EXAMPLE 4

This example demonstrates preparation of a phosphated, oxidized starch per this invention.

Corn starch was oxidized as described in preparation Example 1. After the bleach was consumed, an 18% solution of STMP was added at a ratio of 0.2:1 (STMP:dry starch), as shown in Table I, by weight of dry starch originally oxidized. The reaction solution was adjusted to pH 10.5 with sodium hydroxide (13% solution), heated to 70°C and maintained at temperature for 45 minutes. Subsequent neutralization with hydrochloric acid followed by precipitation into methanol yielded a product having a carboxyl D.S. of 0.41 containing 4.3% phosphorous of which 0.10% is bound in ester linkages.

The following examples demonstrate the use of oxidized starches and phosphated, oxidized starches.

EXAMPLE 5

The addition of effective concentrations of dispersant to high-solid pastes results in drastic viscosity decreases and transforms them into free-flowing dispersions. This response to dispersant addition was used to evaluate the efficiencies of oxidized starches and phosphated, oxidized starches.

Oxidized and phosphated, oxidized starch compositions were added to high-solid pastes of kaolin clay (70%) or calcium carbonate (75%) either directly in solid form or in aqueous 25% solutions. Addition was accompanied by good mechanical agitation using a high speed stirrer or Gifford-Wood Homogenizer Mixer. The pH of dispersed clay slurries was adjusted to 7.0 to 7.5 by addition of solid sodium carbonate. The slurries were cooled to room temperature before measuring Brookfield viscosities.

Table I shows results obtained with Kaolin clay. Table II shows the results obtained for calcium carbonate.

Table I

Kaolin Clay											
Sample	Starch Type	Oxidation Method as By Example	STMP Ratio ¹	% P, as Ester ²	Product % P, as Salt ³	Carboxyl D.S.	70 % Clay Viscosities ⁴ (cps x 10 ⁻³ Dispersant)				
							0.2	0.3	0.4	0.5	0.6%
A (Control)	Corn	1	0	0	0	0.40	20	14	5.6	4.4	3.4
B (Invention)	Corn	3	0.1:1	0.05	2.3	0.43	11	4	2.4	1.8	2
C (Invention)	Corn	4	0.1:1	0.05	1.9	0.43	11.5	4	1.6	1.4	1.6
D (Invention) ⁵	Corn	3	0.2:1	0.06	3.6	0.45	19	3.8	1.8	1.4	1.6
E (Invention) ⁶	Corn	4	0.2:1	0.10	4.3	0.41	13	4	1.4	1.4	1.4

¹ Ratio of STMP to dry starch (by weight).

² Phosphate bound to the oxidized starch as an ester.

³ Unbound phosphate.

⁴ Brookfield RVT viscosities at 10 rpm using appropriate spindle for slurries treated with indicated levels of dispersant by weight of clay.

⁵ Prepared in Preparation Example 3.

⁶ Prepared in Preparation Example 4.

Table II

Sample	Starch Type	Oxidation Method: as By Example	Calcium Carbonate				75% CaCO ₃ Viscosities ⁴ (cps x 10 ⁻³ Dispersant)				
			STMP Ratio ¹	%P, as Ester ²	Product %P, as Salt ³	Carboxyl D.S.					
							0.2	0.3	0.4	0.5	0.6%
F (Invention)	Waxy Maize	3	0.1:1	0.06	2.3	0.43	10	2	1.4	2	3.5
G (Invention)	Waxy Maize	3	0.1:1	0.06	0.7	0.43	0.08	0.07	0.09	0.12	0.14
H (Comparison)	Waxy Maize	1	0	0	0	0.42	2.6	0.80	0.85	0.88	0.88
I (Comparison)	Waxy Maize	1	0	0	2.4 ⁺⁵	0.42	5.1	6.1	6.8	8.3	25

¹ Ratio of STMP to dry starch (by weight).² Phosphate bound to the oxidized starch as an ester.³ Unbound phosphate.⁴ Brookfield RVT viscosities at 20 rpm using appropriate spindle for slurries treated with indicated levels of dispersant by weight of clay.⁵ Composition blended with a mixture of ortho, pyro and triphosphates.

The results in Table I show that all of the samples perform well, but that phosphated, oxidized starch, Samples BE, perform better than the oxidized starch, Sample A. The phosphated, oxidized starch containing samples had lower viscosity than Sample A at equivalent dispersant concentrations. Thus, phosphated, oxidized starch dispersions are shown to be easier to pump and handle.

Table I also shows that phosphated, oxidized starches are more efficient than their non-phosphated counterparts. This is shown by the fact that less of the phosphated, oxidized starch than the oxidized starch was necessary to achieve a particular viscosity. Specifically, based on the results of Table I, 0.5%-0.6% oxidized starch appears to be necessary to achieve the same viscosity as 0.3% of the phosphated, oxidized starch.

Similar results to those discussed above were achieved with Samples F through I of Table II. However, Samples F and I did not perform as well as other samples due to the large amount of unbound phosphates.

EXAMPLE 6

The relative effect of dispersant on filler retention was assessed by handsheets in which kaolin clay was dispersed with a phosphated, oxidized corn starch composition (prepared as in Example 3 at an STMP ratio of 0.1:1) having a carboxyl D.S. of 0.40. A commercial sodium polyacrylate was used as a control.

Handsheets were made from bleached hardwood kraft beaten to 500 Canadian Standard Freeness (CSF). Clay was added to the pulp at 20 wt. % from 70% stock slurries dispersed at 0.3% (6 lb/ton) with either a phosphated, oxidized starch composition or a commercial sodium polyacrylate dispersant. The pH at the stock chest was 7.3 and a cationically modified polyacrylamide retention aid (powder comprised of 7.0 mole % 2-acryloyloxyethyl trimethylammonium and 93.0 mole % acrylamide, having a 9% moisture content, a Brookfield Viscosity (0.5% solution, #2 spindle) of 250 cps at 25°C and 60 rpm, and a solution pH (0.5% solution) of 4.7) was added to the chest at level of 0, 0.025, 0.05 and 0.7% by weight of pulp. Forty pound basis handsheets were formed with recycled dilution water. Results are shown in Table III.

Table III

Dispersant	Retention Aid, %	Retention of Clay, %
Phosphated, oxidized starch	0	14.2
Phosphated, oxidized starch	0.025	59.4
Phosphated, oxidized starch	0.050	79.1
Phosphated, oxidized starch	0.075	89.3
Sodium polyacrylate	0	11.4
Sodium polyacrylate	0.025	48.8
Sodium polyacrylate	0.050	70.6
Sodium polyacrylate	0.075	82.4

The data in Table III show that better retention is obtained using phosphated, oxidized starch than using sodium polyacrylate at equal concentrations.

EXAMPLE 7

This example shows preparation and use of gumming and fountain solutions per this invention.

A. Gumming Solution

A 16% concentrated solution of phosphated, oxidized starch was prepared at room temperature. Then, 0.1% methyl parasept based on the total weight of the solution, was added to the solution as a preservative. The pH of the solution was lowered to 4.2 using phosphoric acid.

A negative substrate anodized aluminum type plate was then gummed, by pouring a small amount of the above phosphated, oxidized starch gumming solution onto the plate and rubbing it by hand with a cheesecloth. The starch was easy to apply and, after application, no streak marks were observed. The plate was allowed to air dry.

5 To test the desensitizing properties of the starch solution the above plate was then mounted on a printing press (Davidson 501) and 10,000 copies were printed. The printing quality was good and no problems were observed during printing.

10 The ability of the phosphated starch gumming solution to protect the plate during storage was evaluated by cleaning the plate used to make 10,000 copies above with a cleaning solution and regumming it with the same phosphated, oxidized starch gumming solution. The gummed plate was stored for six days in the press-room. Then, twelve hundred copies of paper were printed using this plate and the fountain solution of Sample 5, Table IV below. Again, printing quality was good. The phosphated, oxidized starch gumming solution protected the plate during its storage and did not attack the plate metal.

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B. Fountain Solution

20 Six fountain solutions (one gallon each), having the compositions shown in Table IV below, were prepared using the starch used in the gumming solution of Part A of this Example.

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TABLE IV

Fountain Solutions					
Fountain Solution Formulation				Solution ¹ (pH)	
Solution A (ml)	Solution B (ml)	Water (ml)	Isopropanol (ml)		
28	14	3800	-	4.5 4.2 4.5 4.3 4.6 4.4	
28	10	3800	-		
28	5	3800	-		
28	11	3000	800		
28	10	3000	800		
28	5	3000	800		
Solution A =	90.0 gr. 2.5 gr. 907.5 gr. 1000.0 gr.	zinc nitrate ² phosphoric acid dist. H ₂ O	Solution B =	26.0% 0.1%	phosphated, oxidized starch solution methyl parasept

¹ Additional phosphoric acid was used to lower pH to between 4.0 - 4.5.² Zinc nitrate functions as a corrosion inhibitor.

The performance of the fountain solutions was evaluated while printing 2500 sheets with each (using the plate and gumming solution described in part A of this Example). The printing quality was good and the amount of fountain solution needed was normal. Slightly better performance was observed with the 80/20 water/isopropanol mixture used in samples 4, 5 and 6. Further, although solutions having starch solids contents as low as 1.3 grams (samples 3 and 6) performed well, it is recommended to use at least 2.0 grams phosphated, oxidized starch per gallon of solution.

A scum test was run to identify how efficient the fountain solutions are in desensitizing the plate. Printing was continued after the 2500 sheets, described above, were printed without use of the fountain solution. This caused the non-image areas to become ink receptive and, as a result, the entire plate was covered with black ink. Once the entire plate was covered with ink, the fountain solution supply was restarted and the number of sheets it took to desensitize the non-image area of the plate and to give clear printing were counted. With each of the solutions of Table IV, it took 30 sheets or less. The fountain solutions containing isopropyl alcohol performed slightly better than those only containing water.

Claims

1. An oxidized and depolymerized starch that has a phosphate degree of substitution of at least about 0.0002 and a molecular weight of less than 200,000 Daltons is characterized in that it is phosphated to a phosphate degree of substitution of about 0.002 to about 0.005, has a molecular weight of about 1,500 to about 40,000 Daltons, and is soluble in cold water by virtue of a carboxyl degree of substitution of 0.30 to 0.96.

2. An oxidized and depolymerized starch as claimed in claim 1, further characterized in that it has a carboxyl degree of substitution of 0.44 to 0.50.

3. An oxidized and depolymerized starch as claimed in claim 1 or 2, further characterized in that it has a phosphate degree of substitution of about 0.003 to about 0.005.

4. An oxidized and depolymerized starch as claimed in claim 3, further characterized in that it has a phosphate degree of substitution of about 0.004 to about 0.005.

5. An oxidized and depolymerized starch as claimed in any of the preceding claims, further characterized in that it has a molecular weight of about 5,000 to about 30,000 Daltons.

6. An oxidized and depolymerized starch as claimed in claim 5, further characterized in that it has a molecular weight of about 15,000 to 20,000 Daltons.

7. An oxidized and depolymerized starch as claimed in any of the preceding claims, further characterized in that it is produced from corn, potato, tapioca, sago, rice and wheat starch.

8. An oxidized and depolymerized starch as claimed in claim 7, further characterized in that it is produced from waxy maize or potato starch.

9. Use of an oxidized and depolymerized starch as claimed in claim 1 to control the rheology of an aqueous dispersion containing solid particulates.

10. Use of an oxidized and depolymerized starch as claimed in claim 9 further characterized in that the aqueous dispersion contains the starch in an amount of about 0.2 to about 0.6%, based on the weight of the dispersed particulates.

(19)



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(54) **Phosphated, oxidized starch and use of same as dispersant in aqueous solutions and coating for lithography.**

(57) A novel phosphated, oxidized starch having a molecular weight of about 1,500 to about 40,000 Daltons, a carboxyl degree of substitution of 0.30 to 0.96, and a phosphate degree of substitution of from about 0.0002 to about 0.0005, which is useful as a dispersant for aqueous, high-solid slurries of minerals and inorganic pigments, as a replacement for gum arabic in gumming and fountain solutions for lithography, and as a drilling fluid additive.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 12 0568

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-2 801 242 (CORN PRODUCTS REFINING CO.) * Column 1, lines 20-22; column 3, lines 13-16; example 11 *	1-8	C 08 B 31/18 C 08 B 31/06 B 01 F 17/00 //
Y	* Claims *	9-10	C 11 D 3/37 B 41 M 1/06
D,Y	DE-A-3 203 067 (KEMIRA OY) * Claims *	9-10	D 21 H 3/28
X	CHEMICAL ABSTRACTS, vol. 76, 1972, page 83, abstract no. 26629f, Columbus, Ohio, US; & JP-A-71 06 377 (JAPAN FOOD PROCESSING CO., LTD) 17-02-1971 * Whole abstract *	1-8	
X	CHEMICAL ABSTRACTS, vol. 75, 1971, page 88, abstract no. 65454u, Columbus, Ohio, US; A.I. ZHUSHMAN et al.: "Swollen starch for nutritive purposes", & SAKH. PROM. 1971, 45(6), 58-60 * Whole abstract *	1-8	
A	US-A-3 539 551 (N.E. LLOYD)		TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 08 B
A	FR-A-1 536 160 (BLATTMANN & CO.)		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-06-1989	Examiner LENSEN H.W.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
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